High-pressure speed of sound measurements in methyl nonafluorobutyl ether and ethyl nonafluorobutyl ether

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Abstract

In this work, experimental speed of sound values (*U*) in the compressed liquid phase of methyl nonafluorobutyl ether and ethyl nonafluorobutyl ether from 283.15 to 323.15 K and for pressures ranging up to 100 MPa are presented. The experimental speed of sound data, together with compressed liquid densities in the range between 0.1 to 40 MPa [1] were used to estimate densities and isentropic compressibility of both fluids up to 100 MPa.

Keywords: speed of sound, density, compressibility**,** high pressure, methyl nonafluorobutyl ether, ethyl nonafluorobutyl ether.

1. INTRODUCTION

The continuous search to identify alternatives to the commonly halocarbonated compounds used in industry in applications as refrigeration, foaming, precision cleaning and fire extinguishing has attracted increasing attention on hydrofluoroethers (HFEs) [2-4]. The main reason for this interest is their low impact environmental profile, including zero ozone depletion potential and short atmospheric lifetimes. Nevertheless, experimental thermodynamic data about this family of fluids are still scarce in literature. In order to develop accurate theoretical estimation models to simulate the behaviour of HFEs more experimental information is needed not only on VLE and PVT, but also on other essential thermodynamic properties as heat capacities and sound velocities, which turn out to be an excellent test of accuracy of any theoretical model. In a previous work [1], densities were determined for liquid methyl nonafluorobutyl ether and ethyl nonafluorobutyl ether for pressures up to 40 MPa. In this work, speeds of sound in the temperature range 283.15 to 323.15 K and for pressures up to 100 MPa were determined. Then, using this set of data, density and isentropic compressibility of both fluids was evaluated in the same pressure range by means of an iterative numerical procedure based on the integration of U^{-2}. The procedure which rests on low pressure densities data as initialising values, allows to estimate the density up to 100 MPa.

2. EXPERIMENTAL

Nonafluorobutyl methyl ether and nonafluorobutyl ethyl ether were obtained from TCI. Each one of these products is actually a mixture of inseparable structural isomers, with the same physical properties. The first one has a purity of 99,8% (39.1% of nonafluorobutyl methyl ether ($CF_3(CF_2)_3OCH_3$, CAS No. 163702-07-6) and 60.7% of nonafluoroisobutyl methyl ether ($(CF_3)_2CFCF_2OCH_3$, CAS No. 163702-08-7)), and no purity value is supplied for the second one, composed of nonafluorobutyl ethyl ether ($CF_3(CF_2)_3OCH_2CH_3$, CAS

No. 163702-05-4) and nonafluoroisobutyl ethyl ether ($(CF_3)_2CFCF_2OCH_2CH_3$, CAS No. 163702-06-5). Both chemicals were degassed in an ultrasonic bath before use.

Experimental values of speed of sound were obtained from a high-pressure cell using a pulse echo technique operating at 3 MHz. The experimental technique and the measuring device have been previously described in detail [5-7]. This measuring device consists of a stainless steel autoclave cell closed at both ends by two identical buffers which act as connecting medium between the piezo-electric transducers and the fluid. The ultrasonic speed is obtained through the direct measurement of the transit time of the pulse through the sample using a Gould numerical oscilloscope, taking into account the variation of the inner distance in the cell with both temperature and pressure. The cell is placed in a circulating bath that combines oil and airflow to thermostatize the sample, and the temperature is measured directly inside the cell with a platinum probe. Pressure is controlled by a double cylinder pump connected to a pressure multiplier that allows to reach pressures up to 100 MPa, and measured with an HBM manometer, which calibration is checked periodically through a Bunderberg dead weight tester. An evaluation of uncertainties in time determination, as well as in pressure and temperature determination yield a maximum uncertainty of 0.2% over the whole temperature and pressure range. This accuracy value has been checked in previous works [5,7] through comparison with recommended speed of sound values of several alkanes.

3. RESULTS AND DISCUSSION

Speed of sound *U* was determined for both HFEs from 283.15 to 323.15 K and from atmospheric pressure to 100 MPa. Experimental values are listed in Table I. Experimental speed of sound values were fitted using the following rational expression depending on temperature and pressure:

$$\left\{U/(m\cdot s^{-1})\right\}^{-2} = \left\{A + B(p/MPa) + C(p/MPa)^2 + D(p/MPa)^3\right\} / \left\{E + F(p/MPa)\right\} \quad (1)$$

where

$$A = \sum_{i=0}^{n} A_i (T/K)^i \quad (2)$$

$$E = 1 + E_1 (T/K) \quad (3)$$

with n=3 in Eq. 2. Thus, A_i, B, C, D, E_1 and F are the nine fitting parameters, listed for both compounds in Table 3, together with the obtained average absolute deviations (AAD) and average percent deviations (APD). Figure 1 shows the experimental speed of sound values plotted vs. pressure for each isotherm, together with the fitting curves.

The experimental set of values of speed of sound at pressures up to 100 MPa can be used to extend the experimental density values published previously [1] in the range 0.1 to 40 MPa, allowing to obtain an estimation of density behaviour up to 100 MPa. The iterative calculation procedure has been described in detail in [8], and is based on the existing relation between the isothermal compressibility factor κ_T and the isentropic compressibility factor κ_S:

$$\kappa_T = \kappa_S + \frac{T\alpha^2}{\rho C_p} \tag{4}$$

where α stands for the thermal expansion coefficient and C_p represents the isobaric specific heat. Taking into account in adition the Laplace equation for the isentropic compressibility factor:

$$\kappa_S = \left(\rho U^2\right)^{-1} \tag{5}$$

and considering the absence of dispersion effects at the working frequency (3 MHZ) in the studied fluids, that allows to identify the ultrasonic velocity with the speed of sound, substitution of Eq. 2 into Eq. 1 and integration over a range of pressure at constant temperature yields the following expression:

$$\rho(p,T) = \rho(p_i,T) + \int_{p_i}^{p} U^{-2} dp + T\int_{p_i}^{p} \frac{\alpha^2}{C_p} dp \tag{6}$$

where p_i is a reference pressure, considered in this case to be 0.1013 MPa. This expression allows to calculate high pressure densities from ultrasonic measurements for a fluid provided that density as well as heat capacity at a reference pressure is known. In the present work, the reference density data were taken from [1] and were smoothed as a function of temperature using cubic polynomial functions. The isobaric expansion coefficient, present in the last integral, is determined at each pressure step by differentiation of density with respect to temperature whereas the heat capacity is found at each stage of the calculation from:

$$C_p(p,T) = C_p(p_0,T) - \int_{p_0}^{p} T\left[\alpha_P{}^2 + (\partial\alpha_P / \partial T)_p\right] / \rho dp \tag{7}$$

Nevertheless, C_p values at reference pressure for these HFEs were not available in literature, so an alternative predictor corrector algorithm [8] was applied to calculate densities above 40 MPa. The first step of this method consists in predicting C_p at atmospheric pressure through Eq. 4. Using the estimate value of Cp densities up to 40 MPa are calculated and then compared to the experimental data. In a second step the heat capacity values are corrected in order to fit with experimental density values at 40 MPa. After this optimisation is achieved, estimation of density is extended up to 100 MPa. Results are summarized in Table III and plotted in Figure 2, together with experimental values up to 40 MPa. The estimation of the density trend with pressure obtained with this method is fairly good, and for instance the deviation in the range 0.1-40 MPa of the estimated values if compared with the experimental ones shows an APD (%) of $4{\cdot}10^{-3}$ for methyl nonafluorobutyl ether and $7{\cdot}10^{-3}$ for ethyl nonafluorobutyl ether. (AAD of $7{\cdot}10^{-2}$ $Kg{\cdot}m^{-3}$ and 0.1 $Kg{\cdot}m^{-3}$, respectively). This method allows obtaining a good estimation of the volumetric behaviour of both fluids beyond the working range of the high-pressure densimeter. Once these estimated density values are obtained, Eq. 5 can be used to determine the isentropic compressibility factor in the full pressure range 0.1-100 MPa . These has been listed in Table IV and plotted for both fluids in Figure 3.

CONCLUSIONS

Experimental speed of sound for methyl nonafluorobutyl ether and ethyl nonafluorobutyl ether are presented from 283.15 to 323.15 K at pressures up to 100 MPa. An iterative numerical method has been then applied to extend former experimental values of compressed liquid densities up to 40 MPa, obtaining density estimation in the range 40-100 MPa. This method provides information of the volumetric behaviour of both HFEs beyond the operative range of the vibrating tube densimeter used in [1]. This density estimation enables isentropic compressibility factor calculation in the same pressure range.

The information provided in this study together with future works devoted to the experimental high-pressure isobaric heat capacity of liquid HFEs will contribute to an adequate thermophysical characterization of such substances.

List of symbols

A_i Fitting coefficient in Eq. 2
AAD Absolute Average Deviation
APD Average Percent Deviation
B Fitting coefficient in Eq. 2
C Fitting coefficient in Eq. 2
C_P Isobaric heat capacity
D Fitting coefficient in Eq. 2
E_1 Fitting coefficient in Eq. 2
p Pressure
p_i Reference pressure (0.1 MPa) of Eq 6.
T Temperature
U Speed of sound

Greek symbols

α Thermal expansion coefficient
κ_T Isothermal compressibility
κ_S Isentropic compressibility
ρ Density

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TABLES

Table I: Experimental speed of sound values u ($m \cdot s^{-1}$) for methyl nonafluorobutyl ether and ethyl nonafluorobutyl ether:

Methyl nonafluorobutyl ether						
T (K) / p (MPa)	283.15	293.15	298.15	303.15	313.15	323.15
0.1	650.5	617.0	600.2	584.0	551.7	519.6
5	682.2	650.0	634.7	619.3	589.1	559.7
10	711.1	680.3	666.0	651.7	623.4	595.7
15	737.9	708.3	694.4	680.9	653.3	627.8
20	762.6	734.0	720.6	707.5	681.8	656.9
30	808.4	781.9	769.2	756.6	732.7	709.3
40	850.1	824.8	812.6	800.9	777.9	756.1
50	888.2	864.1	852.4	841.3	819.1	797.6
60	923.6	900.6	889.2	878.2	856.7	836.7
70	957.0	934.6	923.2	912.6	891.8	872.4
80	988.4	966.7	955.5	945.1	924.7	905.8
90	1017.8	997.0	985.9	975.8	955.9	937.3
100	1046.5	1025.6	1015.0	1004.9	985.5	967.2
Ethyl nonafluorobutyl ether						
T (K) / p (MPa)	283.15	293.15	298.15	303.15	313.15	323.15
0.1	669.9	638.2	622.6	607.4	575.5	544.2
5	703.6	672.9	657.3	642.8	614.2	585.8
10	732.8	703.3	689.6	675.1	648.3	621.9
15	759.2	731.8	718.7	705.1	679.2	654.2
20	785.5	758.0	745.7	732.7	707.6	683.7
30	830.5	806.0	793.2	782.1	758.4	736.6
40	871.6	849.5	836.9	826.3	804.2	783.4
50	910.1	888.8	877.1	867.0	846.1	825.9
60	946.8	925.5	914.2	904.4	884.1	864.7
70	980.7	959.8	948.8	939.2	919.6	900.7
80	1012.5	992.0	981.7	971.8	952.7	934.6
90	1042.2	1022.1	1013.0	1002.7	984.3	966.3
100	1070.5	1051.4	1041.1	1032.4	1014.2	996.5

Table II: Correlation coefficients for eqs. 1-3, speed of sound absolute average deviations (AAD, $m \cdot s^{-1}$), and average percent deviations (APD, %):

	Methyl nonafluorobutyl ether	Ethyl nonafluorobutyl ether
$A_0/(m^{-2} \cdot s^2)$	$-1{,}59456 \cdot 10^{-6}$	$-2{,}27482 \cdot 10^{-7}$
$A_1/(m^{-2} \cdot s^2 \cdot K^{-1})$	$1{,}68780 \cdot 10^{-8}$	$4{,}45422 \cdot 10^{-9}$
$A_2/(m^{-2} \cdot s^2 \cdot K^{-2})$	$-4{,}03869 \cdot 10^{-11}$	$-3{,}04688 \cdot 10^{-12}$
$A_3/(m^{-2} \cdot s^2 \cdot K^{-3})$	$3{,}81029 \cdot 10^{-14}$	$6{,}43907 \cdot 10^{-16}$
$B/(m^{-2} \cdot s^2 \cdot MPa^{-1})$	$7{,}94767 \cdot 10^{-9}$	$8{,}86527 \cdot 10^{-9}$
$C/(m^{-2} \cdot s^2 \cdot MPa^{-2})$	$-5{,}12490 \cdot 10^{-6}$	$-5{,}68081 \cdot 10^{-11}$
$D/(m^{-2} \cdot s^2 \cdot MPa^{-3})$	$1{,}83443 \cdot 10^{-13}$	$1{,}97954 \cdot 10^{-13}$
E_1/K^{-1}	$-2.32089 \cdot 10^{-3}$	$-2.25659 \cdot 10^{-3}$
F/MPa^{-1}	$1.05322 \cdot 10^{-2}$	$1.15064 \cdot 10^{-2}$
$AAD/(m \cdot s^{-1})$	0.31	0.35
APD/%	$3.8 \cdot 10^{-2}$	$4.3 \cdot 10^{-2}$

Table III. Density ρ ($kg \cdot m^{-3}$) Deduced from Ultrasonic Measurements for methyl nonafluorobutyl ether and ethyl nonafluorobutyl ether.

Methyl nonafluorobutyl ether					
T (K) / p (MPa)	283.15	293.15	298.15	303.15	313.15
40	1643.22	1624.64	1615.36	1606.10	1587.70
50	1659.65	1641.99	1633.17	1624.39	1606.97
60	1674.70	1657.80	1649.37	1640.98	1624.38
70	1688.59	1672.35	1664.26	1656.20	1640.28
80	1701.53	1685.85	1678.05	1670.29	1654.95
90	1713.64	1698.47	1690.92	1683.41	1668.60
100	1725.06	1710.34	1703.01	1695.73	1681.38

Ethyl nonafluorobutyl ether						
T (K) / p (MPa)	283.15	293.15	298.15	303.15	313.15	323.15
40	1539.52	1523.05	1514.82	1506.61	1490.28	1474.17
50	1554.97	1539.25	1531.40	1523.59	1508.08	1492.81
60	1569.16	1554.06	1546.54	1539.05	1524.20	1509.62
70	1582.29	1567.73	1560.48	1553.26	1538.98	1524.98

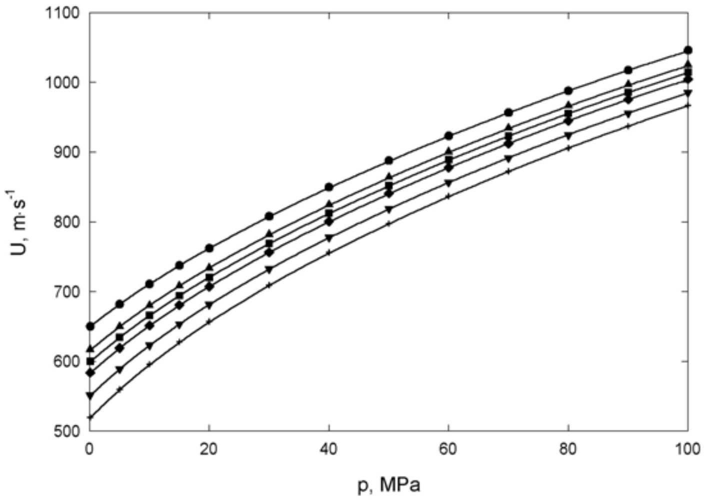
80	1594.54	1580.44	1573.42	1566.44	1552.65	1539.14
90	1606.04	1592.34	1585.53	1578.76	1565.38	1552.31
100	1616.88	1603.55	1596.92	1590.34	1577.33	1564.63

Table IV. Isentropic Compressibility κ_S (GPa^{-1}) deduced from Ultrasonic Measurements.

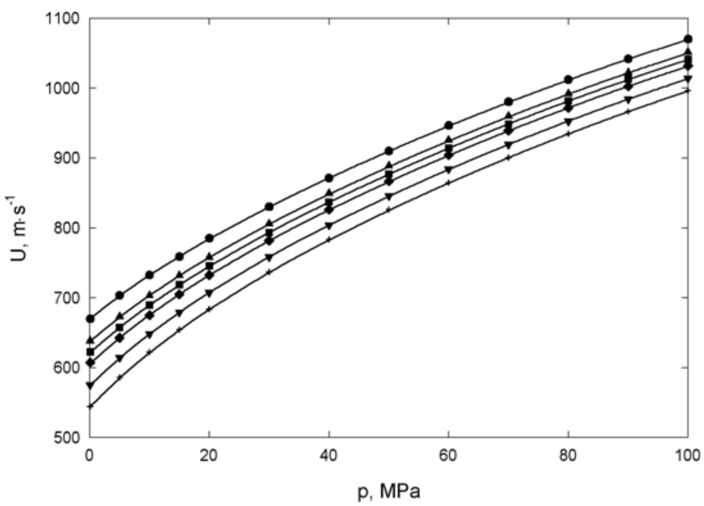
Methyl nonafluorobutyl ether					
T (K) / p (MPa)	283.15	293.15	298.15	303.15	313.15
0.1	1.520	1.720	1.832	1.953	2.228
10	1.250	1.385	1.458	1.535	1.704
20	1.071	1.170	1.222	1.277	1.395
30	0.942	1.019	1.059	1.101	1.190
40	0.843	0.906	0.938	0.971	1.041
50	0.765	0.817	0.843	0.871	0.928
60	0.700	0.744	0.767	0.790	0.838
70	0.647	0.685	0.704	0.724	0.765
80	0.601	0.635	0.652	0.670	0.705
90	0.563	0.593	0.608	0.623	0.655
100	0.530	0.557	0.571	0.585	0.613

Ethyl nonafluorobutyl ether						
T (K) / p (MPa)	283.15	293.15	298.15	303.15	313.15	323.15
0.1	1.526	1.711	1.815	1.926	2.176	2.471
10	1.258	1.381	1.449	1.520	1.674	1.849
20	1.080	1.171	1.220	1.270	1.378	1.497
30	0.953	1.023	1.060	1.099	1.181	1.269
40	0.855	0.912	0.942	0.972	1.037	1.106
50	0.776	0.824	0.849	0.874	0.927	0.983
60	0.712	0.752	0.773	0.795	0.839	0.886
70	0.658	0.693	0.711	0.730	0.768	0.808
80	0.612	0.643	0.659	0.675	0.709	0.743
90	0.573	0.601	0.615	0.629	0.659	0.689
100	0.540	0.565	0.578	0.590	0.617	0.644

FIGURES

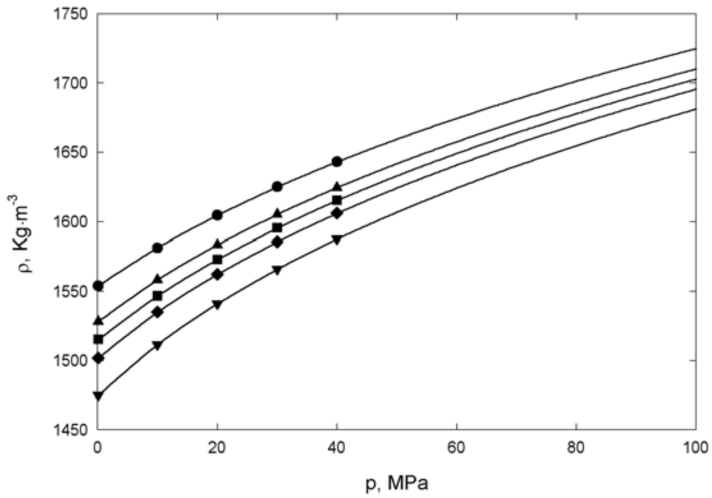


(a)



(b)

Figure 1: Experimental speed of sound data (U/ m·s^{-1}), for methyl nonafluorobutyl ether (a) and ethyl nonafluorobutyl ether (b), at: ● 283.15 K, ▲ 293.15 K, ■ 298.15 K, ♦ 303.15 K, ▼ 313.15 K, + 323.15 K, and correlation with equation 1 (solid line).



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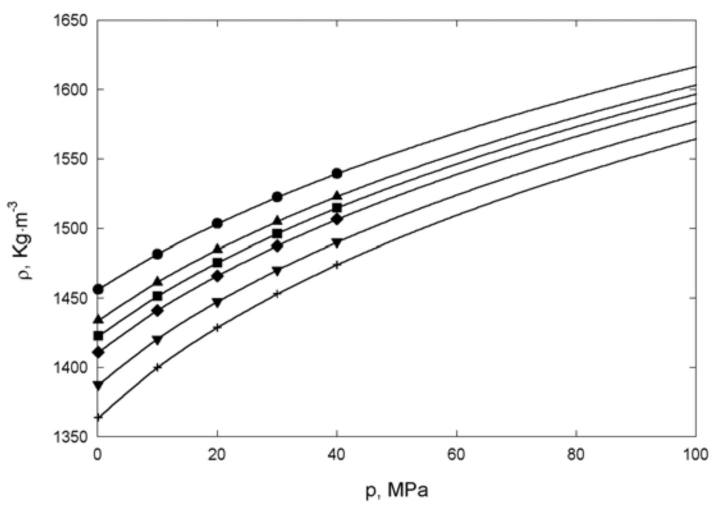

(b)

Figure 2: Experimental density data (ρ/ Kg·m^{-3}, [1]), for methyl nonafluorobutyl ether (a) and ethyl nonafluorobutyl ether (b), at: ● 283.15 K, ▲ 293.15 K, ■ 298.15 K, ♦ 303.15 K, ▼ 313.15 K, + 323.15 K, compared with estimated values obtained through the described iterative method (solid line).

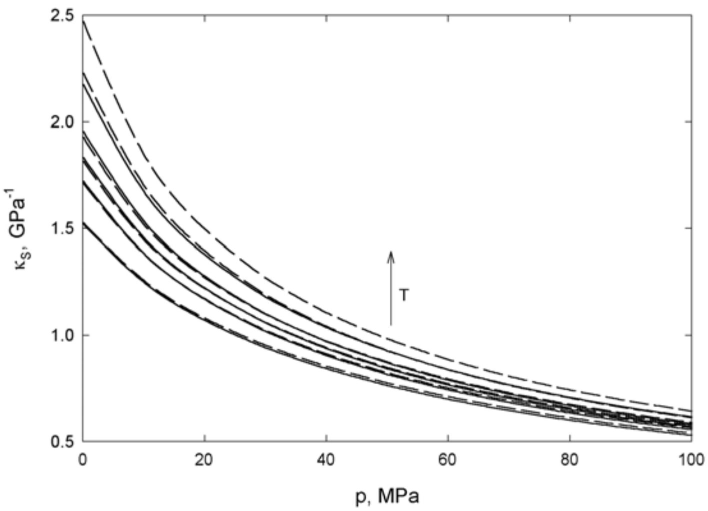

Figure 3: Isentropic compressibility factor (κ_S, GPa^{-1}), calculated from experimental speed of sound and estimated densities for each isotherm, for methyl nonafluorobutyl ether (solid line, 283.15-313.15 K) and ethyl nonafluorobutyl ether (dashed line, 283.15-323.15 K).